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GB A 2153851 GB A 2153393 EP A2 0146323
US 4632870 US 4595631 US 4567116
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Selected US specifications from IPC sub-classes C23C G11B

(54) Magnetic recording media

(57) A magnetic recording medium eg tape employing a ferromagnetic film as the magnetic layer has a non-magnetic metal and/or a non-magnetic metal oxide diffused into the ferromagnetic film along the direction of film thickness, so that the concentration distribution is substantially uniform. The non-magnetic metal and/or the non-magnetic metal oxide may exist unevenly in the crystal grain boundaries of the ferromagnetic film. The ferromagnetic film may contain at least one of Co, Ni, Fe whilst the non-magnetic metal may be at least one of Bi, Sb, Pb, Sn, Ga, In, Cd, Ge, Si and Tl. The diffused layer is formed by sputtering at a temperature not lower than 150°C with the sputtering pressure usually set so as to be not higher than 1×10^{-2} Pa. In the specific example a Ni-p plated aluminium substrate is subjected to successive sputtering at 160°C and an argon pressure of 4×10^{-1} Pa with Bi, a Co-Ni film and a carbon protective film and film structure analysis showed that the ferromagnetic film comprises non-magnetic Bi diffused into the space between Co-Ni crystals.

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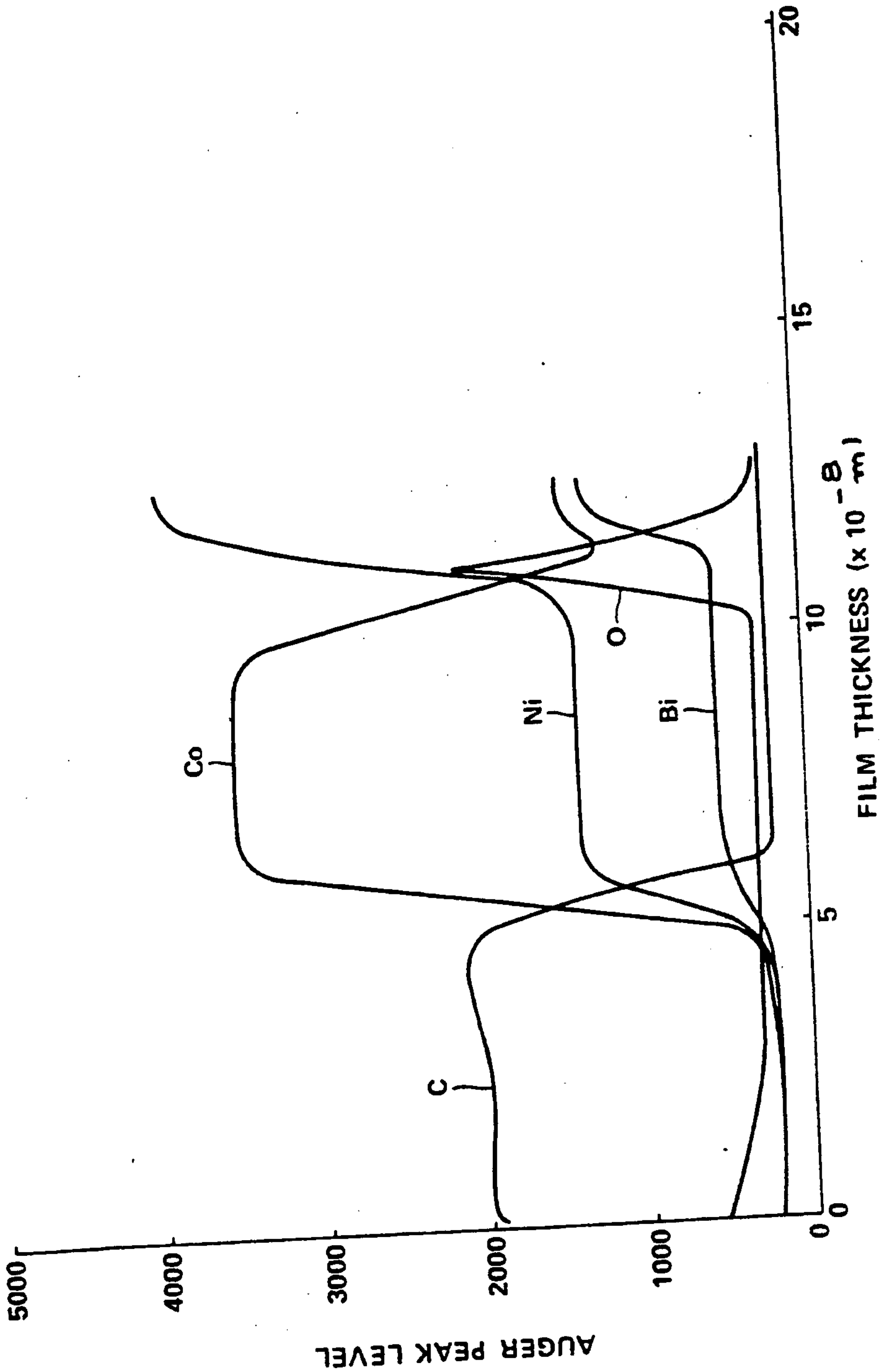

FIG. 1

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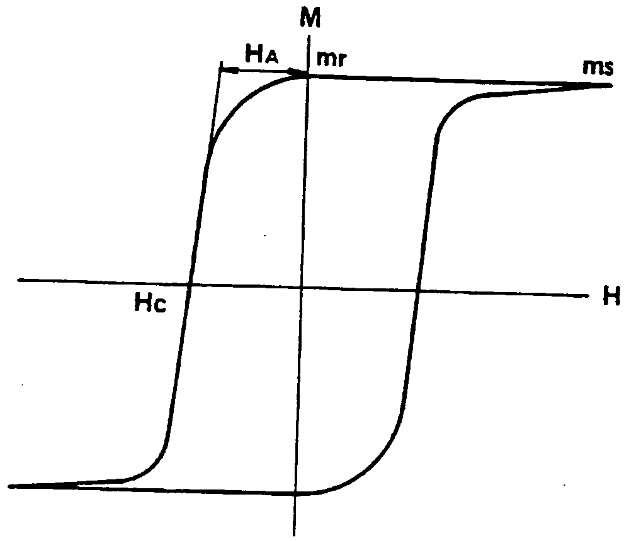

FIG.2

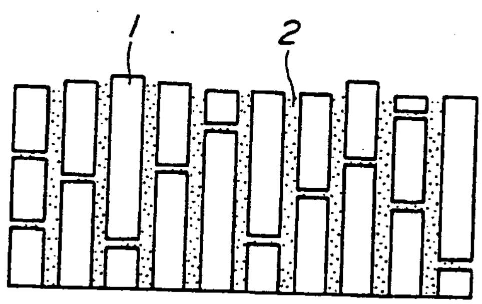

FIG.3

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MAGNETIC RECORDING MEDIA

This invention relates to magnetic recording media.

In the field of magnetic recording, there is pressure to improve the recording density. It has therefore been proposed to use a magnetic recording medium employing a ferromagnetic film as the magnetic layer (hereafter referred to as a thin film type magnetic recording medium), instead of the usual coating type magnetic recording medium.

A thin film type magnetic recording medium is formed by depositing the ferromagnetic metal material, such as Co-Ni, on the substrate as a thin film by physical vapour deposition such as a vacuum evaporation method, to form a magnetic layer. Since a high molecular weight binder is not used, unlike in a coating type magnetic recording medium, a high residual magnetic flux density is obtained, while a high output and superior response to short wavelength characteristics can be obtained, since an extremely thin ferromagnetic film can be used. However, it is difficult to achieve the required coercive force by simply evaporating the ferromagnetic metal material, such as Co-Ni, on the non-magnetic substrate, so that it is usual to form the ferromagnetic film by oblique evaporation, although this reduces the evaporation efficiency.

In the case of a disc-shaped magnetic recording medium, problems occur because of the orientation characteristics obtained with oblique evaporation. While these orientation characteristics are acceptable to some extent with an elongated magnetic recording medium such as a magnetic tape, in a disc-shaped medium they result in increased modulation in the envelope waveform of the playback output.

We have proposed a magnetic recording medium in Japanese laid-open patent publication no 204831/1986, wherein a low melting point non-magnetic metal is deposited first as a film, and then a ferromagnetic metal material is deposited as a film from a substantially perpendicular direction by vacuum evaporation. This method has better evaporation efficiency, and required orientation characteristics and coercive force can be obtained.

Higher rectangular characteristics for the hysteresis loop are required of magnetic recording media employed for digital magnetic

recording technology in, for example, data recording. This means that the distribution of the coercive force is uniform.

According to the present invention there is provided a magnetic recording medium wherein a non-magnetic metal and/or a non-magnetic metal oxide are diffused into a ferromagnetic film formed on a substrate, so that the concentration distribution is substantially uniform along the film thickness direction.

We have found that the state of distribution of the non-magnetic metal or metal oxide in the ferromagnetic film is critical.

The invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 is a characteristic diagram showing the concentration distribution along the film thickness of the ferromagnetic film of the Example, as measured by Auger analysis;

Figure 2 is a characteristic diagram showing a magnetization curve for explaining the measured magnetic characteristics; and

Figure 3 is a schematic view showing the film structure of the ferromagnetic film of the Example.

As the ferromagnetic metal material that forms the ferromagnetic film of the magnetic layer, in embodiments of magnetic recording medium according to the present invention, any material customarily employed in this type of the medium may be employed, including metals such as Fe, Co or Ni, Co-Ni alloys, Fe-Co alloys, Fe-Co-Ni alloys, Fe-Co-B alloys or Co-Ni-Fe-B alloys, occasionally admixed with metal elements, such as Cr, Al, Pt, Ta, W or V.

The non-magnetic metals diffused into the ferromagnetic film may include Bi, Sb, Pb, Sn, Ga, In, Cd, Ge, Si or Tl.

Into the ferromagnetic film, there are diffused the non-magnetic metals and/or oxides of these non-magnetic metals, with the distribution of the concentration thereof being uniform along the film thickness. Although the distribution of the concentration is said to be uniform, these non-magnetic metals do not exist as a solid solution in the ferromagnetic film, but the non-magnetic metal exists unevenly in the grain boundary of, for example, Co-Ni crystal grains such that the distribution of the concentration as a whole is substantially uniform along the film thickness. The size of the crystal grains (so-called grain size) of the ferromagnetic metal material constituting

the ferromagnetic film is preferably in the range of several tens to 200 x 10^{-10}m. With too large a grain size, the crystal grain may turn out to be a grain with multiple magnetic domains, resulting in increased magnetic interaction and reduced coercive force.

In order to provide such a film structure, the ground layer of the non-magnetic metal is previously formed and a ferromagnetic film may be deposited by sputtering on this ground layer. In practice the film thickness of the ferromagnetic film may be 100 to 3000 x 10^{-10}m and is preferably in the range of 400 to 1000 x 10^{-10}m.

During sputtering of the ferromagnetic film, an optimum coercive force distribution may be obtained by adjusting the sputtering conditions, while electromagnetic conversion characteristics are also better than those obtained by evaporation.

For example, the substrate temperature during the sputtering is preferably not lower than 150°C. With the temperature not higher than 150°C, prescribed diffusion does not occur, while the magnetic characteristics of the ferromagnetic film produced are deteriorated. Moreover, it is difficult to obtain a required coercive force.

The power is preferably not lower than 1000 W/62.5 cm^2. With the power not lower than this value, the aforementioned film structure is formed. Conversely, with the power less than this value, the sputtered particles have reduced energy, so that sufficient diffusion does not take place and the concentration of the non-magnetic metal becomes higher at the substrate side, so that it again becomes difficult to obtain the prescribed magnetic characteristics.

The sputtering pressure (Ar gas pressure) is only sufficient if it allows normal sputtering to occur and is usually set so as to be not higher than 1 x 10^{-2} Pa. The value of the sputtering pressure differs slightly with the sputtering system employed. For example, the pressure is set so as to be equal to about 10^{-2} to 10^{-1} Pa and 10^{-1} to 1 Pa for RF sputtering and DC sputtering, respectively.

The ground layer of non-magnetic metal is about 40 to 100 x 10^{-10}m thick, depending on the method employed, such as sputtering or vacuum evaporation, but it is preferably formed by sputtering.

If the vacuum of the apparatus is broken after deposition of the non-magnetic metal, the surface of the non-magnetic metal layer is

oxidized, which suppresses the diffusion. It is therefore preferred that the vacuum be maintained until the ferromagnetic film has been deposited by sputtering.

In accordance with the above method, the non-magnetic metal is diffused into the ferromagnetic film and a film structure is provided in which the non-magnetic metal is unevenly present at the grain boundary of the Co-Ni crystal grains. In this case, it is preferred that the ground layer of non-magnetic metal be completely diffused, however, it may remain slightly, although the in-plane distribution of the non-magnetic metal is preferably substantially uniform.

For forming the film structure, in addition to the aforementioned method of sputtering the ferromagnetic film on the non-magnetic metal film as the ground layer, a method may also be employed in which the non-magnetic metal and the ferromagnetic metal material are sputtered or evaporated simultaneously. However, in this case, the non-magnetic metal (such as Bi) and the ferromagnetic metal (such as Co-Ni) are simply mixed together, so that magnetically it becomes difficult to obtain the required coercive force.

Although the present invention can be applied to all kinds of magnetic recording media, such as tape or disc-shaped media, the effect is most beneficial for disc-shaped magnetic recording media.

The non-magnetic substrate may be a resilient high polymeric substrate typified by polyethylene terephthalate, polyethylene naphthalate, aromatic polyamide resin or polyimide, or a rigid substrate such as silicon, glass or light metals, such as aluminium, inclusive of alloys thereof. Above all, when using rigid substrates for a so-called hard disc, it is preferred that a substrate having minute projections and recesses on the surface thereof be employed. For example, when using a substrate formed with recesses about 0.1×10^{-6}m or less in diameter and 0.03×10^{-6}m in depth on the surface thereof, such as chromate alumite substrate, the ferromagnetic film is comminuted magnetically by the minute surface structure resulting in a higher signal-to-noise ratio.

It is noted that the magnetic recording medium comprises the aforementioned substrate and the ferromagnetic film, but a well-known back-coat layer, base layer or top coat layer, including lubricant or rust-proofing agent, may sometimes be provided as required. With a

hard disc, a hard protective film may be formed, such as a carbon protective film.

The overall operation is as follows. When the ferromagnetic film (such as Co-Ni film) is sputtered on the ground layer composed of non-magnetic metal (such as Bi), the substrate temperature is high, while the Bi film is mobile, so that the Bi atoms are diffused into the co-Ni film. Because of the large size of the Bi atoms, diffusion occurs not through the Co-Ni lattice, but through the film defects, such as the structurally weakened portions, such as grain boundaries.

Therefore, Bi exists unevenly in the crystal grain boundaries of the Co-Ni film. Thus, the Bi atoms being diffused will be intruded into the structural defects of the Co-Ni film to communitize the Co-Ni film into fine crystal grains.

As a result, from the viewpoint of magnetism, the ferromagnetic Co-Ni grains are communitized by the non-magnetic Bi, so that they exhibit a weaker magnetic interaction, thus acting as fine particles exhibiting only weak interaction between the particles. Also, the Co-Ni crystal grains are communitized down to the single magnetic domain, so that the coercive force is increased.

On the contrary, when the ferromagnetic film and the non-magnetic metal are evaporated or sputtered simultaneously, the concentration distribution of Bi and Co-Ni is uniform from the time of the film is formed. Thus there is no factor of Bi diffusion, both the concentration and heat being the same, so that Bi is mixed simply with Co-Ni. The Co-Ni crystal grains are particles with multiple magnetic domains larger than the single magnetic domain particle, so that the coercive force is reduced.

The present invention will be explained with reference to specific examples.

Example

Employing a dough-nut shaped Ni-P plated aluminium substrate with an outside diameter of 95 mm and an inside diameter of 25 mm, and conditions including a substrate temperature of 160°C and an argon gas pressure of 4×10^{-1} Pa, a Bi ground layer, a Co-Ni film and a carbon protective film were formed in this sequence by sputtering. The film thicknesses of the Bi ground layer, Co-Ni film and the carbon protective film were 55, 550 and 350×10^{-10}m, respectively. The

film composition for the Co-Ni film was 65 atom % for Co and 35 atom % for Ni.

Comparative Example

Employing the same substrate as that used in the preceding Example, and a substrate temperature of 160°C in a vacuum evaporator, a Bi ground layer, a Co-Ni film and a carbon protective film having film thicknesses of 55, 550 and 350 x 10^{-10}m, respectively, were formed in this sequence.

Static magnetic properties were then measured for magnetic discs according to the Example and the Comparative Example. The static magnetic properties measured were the coercive force Hc, rectangular ratio Rs, coercive force rectangular ratio S*, residual magnetization mr and saturation magnetization ms. The rectangular ratios Rs and S* were found by the following equation on the basis of the values Hc, HA, mr and ms shown in Figure 2.

$$Rs = (mr/ms) \times 100\ (\%) \qquad \ldots(1)$$

$$S^* = (HA/HC) \times 100\ (\%) \qquad \ldots(2)$$

The results are shown in Table 1.

Table 1

	Hc (Oe)	Rs (%)	S* (%)	resid.magn. (emu)	sat.magn. (emu)
Ex.	680	86.6	93.4	3.71×10^{-3}	4.28×10^{-3}
Comp. Ex.	605	82.8	82.8	4.08×10^{-3}	4.68×10^{-3}

(In the table, the values for residual and saturation magnetization are those per unit area, and 1 Oe equals 79.6 A/m.)

The electromagnetic conversion characteristics were measured under the following conditions. The electromagnetic characteristics were measured at the outside diameter (OD: 90 ø position) and the inside diameter portion (ID: 56 ø position).

Test head	:	mini-composite type head
Track width Tw	:	18×10^{-6}m
Gap length	:	1×10^{-6}m
Head float	:	0.35×10^{-6}m
Velocity	:	10 m/sec

The recorded current at the outside diameter portion is 56 mA_{p-p}, while that at the inside diameter portion is 40 mA_{p-p}. As the measurement procedure, a signal at 1.25 MHz (1F) was recorded to find the track averaged amplitude (TAA), then a signal of 2.5 MHz (2F) was recorded, the track averaged amplitude TAA was found and RES was calculated in accordance with the following equation:

RES = (2F TAA/1F TAA) x 100 (%) ...(3)

The results are shown in Table 2.

Table 2

	OD			ID		
	IF TAA mVp-p	RES (%)	O/W (db)	2F TAA mVp-p	RES (%)	O/W (db)
Ex.	0.53	81	-29	0.25	63	-33
Comp. Ex.	0.58	76	-32	0.20	50	-32

From Tables 1 and 2 the difference between the static magnetic and electromagnetic conversion characteristics of the two kinds of magnetic discs is apparent. In particular, in the Examples wherein the ferromagnetic film was deposited by sputtering, the electromagnetic conversion characteristics (RES) are markedly improved.

In order to determine whether or not this difference is due to the difference in the film structure, an elemental analysis in the film thickness direction was conducted by Auger analysis. It was revealed that the film structure including the deposited ferromagnetic

film produced by sputtering exhibited substantially constant Co, Ni and Bi concentrations in the film thickness direction, as shown in Figure 1. From this may be presumed that the film obtained by sputtering exhibits a more uniform composition along the film thickness direction, so that the film exhibits similarly uniform magnetic characteristics.

Moreover, for clarifying the causes of the isotropic high coercive force of the ferromagnetic film, the film structure analysis was made by observation through a transmission electron microscope. It was thus revealed that, as shown in Figure 3, the film structure of the ferromagnetic film may be described as non-magnetic amorphous Bi(2) (inclusive of oxides) diffused into the space between the Co-Ni crystal grains (1).

CLAIMS

1. A magnetic recording medium wherein a non-magnetic metal and/or a non-magnetic metal oxide are diffused into a ferromagnetic film formed on a substrate, so that the concentration distribution is substantially uniform along the film thickness direction.

2. A medium according to claim 1 wherein the non-magnetic metal and/or the non-magnetic metal oxide exists unevenly in the crystal grain boundaries of the ferromagnetic film.

3. A medium according to claim 1 wherein the ferromagnetic film has been formed by sputtering on a ground layer of the non-magnetic metal.

4. A medium according to claim 3 wherein the substrate temperature during said sputtering was not lower than 150°C.

5. A medium according to claim 1 wherein the ferromagnetic film contains at least one of Co, Ni and Fe.

6. A medium according to claim 1 wherein the non-magnetic metal is at least one of Bi, Sb, Pb, Sn, Ga, In, Cd, Ge, Si and Tl.

7. A medium according to claim 1 wherein the non-magnetic metal is Bi.

8. A magnetic recording medium according to claim 1 and substantially as hereinbefore described.

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